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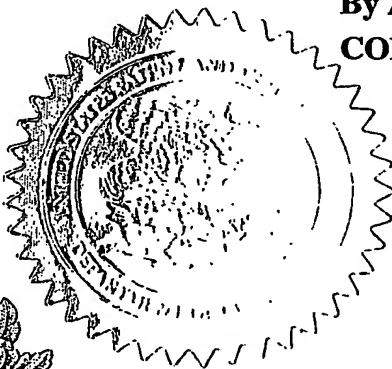
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TITLE OF THE INVENTION (500 characters max)					
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Respectfully submitted,

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PROCESS FOR POLYMERIZING STYRENE MONOMER

The invention relates to a process for polymerizing styrene monomer for the preparation of styrene-containing (co)polymers, wherein the process comprises the steps of continuously or semi-continuously dosing initiator ("first" initiator) to a composition and addition of another initiator ("second" initiator) which is different to the "first" initiator. The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.

Processes for polymerizing styrene monomers are known in the art, for instance from US 5189069, wherein initiators were continuously dosed together with styrene monomer to obtain styrene beads with controlled particle size. It was described that previous to the continuous dosing of the initiator a pre-polymer was prepared by polymerizing a part of the styrene monomers. This preparation is performed without the addition of initiator, necessitating the use of high reaction temperatures. A similar method of making a styrene pre-polymer has been described in US 5905096 and US 6152658. Comparable results have been obtained in EP 0234705 and in EP 0488025, wherein use was made of a different method, i.e. the seeding of the reaction mixture with substantial amounts of polymer seed particles before starting the continuous addition of a mixture of initiator and monomers. All these methods are aimed at particle size control but they suffer from the disadvantage that pre-determining the molecular weight of the polymer and controlling the rate of polymerization is difficult, if not impossible. In addition, these methods require a long polymerization time.

It is an objective of the invention to provide a method of polymerizing styrene monomer for the preparation of styrene based (co)polymer, also referred to in the this description as "polystyrene", with good control of the molecular weight and the distribution thereof as in conventional processes but requiring a shorter polymerization time. The present invention deals with the discovery of a method wherein a combination of continuous or semi-continuous dosing of a "first" initiator to a composition comprising styrene monomer, the use of a "second" initiator, and the

choice of a specific temperature profile can be used for good control of the molecular weight and the molecular weight distribution of polystyrene in a polymerization process of styrene monomer and that requires shorter polymerization time compared to conventional polymerization processes.

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To this end the invention relates to the hereinbefore-mentioned process for polymerizing styrene monomer for the preparation of styrene-containing (co)polymers, wherein the process comprises the steps of continuously or semi-continuously dosing "first" initiator to a composition comprising said styrene monomer and addition of
10 "second" initiator which is different to the "first" initiator, wherein the process is not a process for producing expandable styrene-based polymer beads, which comprises adding a low temperature polymerization initiator to an aqueous medium having suspended therein blowing agent-containing expandable styrene-based polymer small particles whose particle sizes have been adjusted so as to have a particle size
15 distribution falling within a mean particle size of about 20% in a proportion of at least half the amount required for polymerization of a styrene-based monomer to be added to the system, adding a blowing agent to the system in an amount enough to inhibit expansion of said expandable styrene-based polymer small particles while the system is heated to a temperature for first stage polymerization, continuously or intermittently
20 adding thereto a styrene-based monomer to which the rest, if any, of said low temperature polymerization initiator and a high temperature polymerization initiator.

It is noted that this process does not require the use of a pre-polymerization process or the addition of seed particles.

25

It is further noted that the indication "first" initiator and "second" initiator does not relate to the relative order of addition, it is merely used to distinguish between the two initiators.

30 The mixture to which the firstly added initiator is added preferably is free or essentially free of polymerized product prior to the addition of firstly added initiator. The term

"essentially free of polymerized product means that at most 1 wt.% of polymerized product is present, based on the combined weight of monomer and polymerized product.

- 5 During the process of dosing of "first" initiator, polymerized product will be formed. Thus, after a certain period of time "first" initiator is dosed to a mixture of monomer and polymerized product. Preferably, the "first" initiator is continuously or semi-continuously added over a period of at least 0.5, more preferably at least 1 hour. When larger quantities of polymer are made in a batchwise fashion, an addition time
10 of up to 5 hours or more is possible, depending on the molecular weight that is required. From a commercial and technical point of view continuous addition of the "first" initiator is preferred over semi-continuous addition of the "first" initiator.

- The dosing of initiators to the reaction mixture can be semi-continuously or
15 continuously over a period of time wherein at least 20%, preferably at least 40%, more preferably at least 70% of the monomers are being polymerized. If a semi-continuous operation is selected there are many (usually 4 or more) moments at the polymerization temperature at which small portions of the initiator are dosed. If so desired, the semi-continuous and continuous operation can be combined, such that
20 the initiator is dosed semi-continuously for certain (longer or shorter) periods of time.

- Most preferably, the "first" peroxide is dosed continuously or semi-continuously from the point in time at which at least 1%, preferably at least 0.5%, more preferably at least 0.1%, most preferably none of the monomers have already been polymerized
25 until at least 70%, preferably at least 80%, more preferably at least 90%, and most preferably essentially all of the monomer is polymerized. "Essentially all is polymerized" means that less than 1000 ppm of monomer is present in the final polymerized product.

- 30 The term "continuous" also includes continuous addition at variable rate and at variable time intervals. The addition of initiator at variable rate is beneficial for using

the cooling capacity of the polymerization reaction in the most optimal way and to prevent a so-called "run away" during the polymerization reaction. The term "semi-continuous" means an addition method wherein many small portions of initiator are added within short intervals, such to approach the continuous addition.

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In one embodiment, the process according to the invention involves the polymerization of styrene-comprising monomer mixtures, further comprising co-monomers. In this embodiment is preferred that the styrene-comprising monomer mixture comprise at least 50% by weight (wt.%) of styrene monomers, based on the weight of all
10 monomer. Co-monomers that can be used are of the conventional type are preferably selected from the group consisting of vinylidene chloride, vinyl acetate, ethylene, propylene, acrylonitrile, butadiene, and (meth)acrylates and includes ethylenically unsaturated polymers, such as polybutadiene and styrene butadiene rubber. More preferably, at least 80 wt.% of the monomers being polymerized are styrene
15 monomers, whereas the most preferred process is a process wherein all monomers are essentially styrene monomers.

In the process according to the invention, one or more "first" initiators may be used and one or more "second" initiators may be used, as long as essentially all of "first" and "second" initiators that are used fulfill the half-life requirement as presented below.
20 The one or more "first" initiators are dosed into the polymerization reaction mixture at a reaction temperature at which the half-life of each of the "first" initiators preferably is less than 120 minutes, more preferably less than 60 minutes, even more preferably less than 30 minutes, and most preferably less than 10 minutes, and preferably more
25 than 0.05 minutes, more preferably more than 0.5 minutes, even more preferably more than 2.5 minutes, and most preferably more than 5 minutes which reaction temperature is in any case 170°C or lower. The one or more "second" initiators are added to the polymerization mixture at a reaction temperature at which also the half-life of each of the "second" initiators preferably is less than 120 minutes, more
30 preferably less than 60 minutes, even more preferably less than 30 minutes, and most preferably less than 10 minutes, and preferably more than 0.05 minutes, more

preferably more than 0.5 minutes, even more preferably more than 2.5 minutes, and most preferably more than 5 minutes, which reaction temperature is in any case 170°C or lower. Preferably, the reaction temperature is 150°C or lower, more preferably 130°C or lower, and most preferably 120°C or lower. The one or more

- 5 "second" initiators are added to the polymerization mixture at once or they are dosed to the polymerization mixture.

Typically, reaction temperatures are from 60°C to 170°C. Depending on the actual time-temperature-profile, which often depends on the reactor-design, the proper
10 initiators are to be selected on the basis of the half-lives as defined below.

Examples of suitable classes of "first" initiators are peroxydicarbonates, peroxycarbonates, peroxyesters, peroxyketals, diacylperoxides, dialkylperoxides, azo-initiators, and ketone peroxides, and mixtures thereof. The "first" initiators may be
15 mono-, bi-, and polyfunctionalized with peroxy and/or azo moieties. Optionally, the "first" initiators may be further functionalized with amines, phosphates, esters, ethers, alcohols, etc. The "first" initiators are preferably selected from the group consisting of dilauroyl peroxide, dibenzoylperoxide, tert-butyl peroxyperpivalate, tert-amyl peroxy
20 perpivalate, azobis(isobutyronitrile), azobis(2-methylbutyronitrile), tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-butylperoxy)cyclohexane, cumyl peroxyneodecanoate, di(sec-butyl peroxy)neodecanoate, di(2-ethylhexyl) peroxydicarbonate, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, 1,1,3,3-tetramethylbutyl peroxyperpivalate, 1,1,3,3-
25 tetramethylbutyl peroxyneodecanoate, 2,2-di[4,4-di(tert-butylperoxy)cyclohexyl]-propane, tert-amylperoxy-2-ethylhexyl carbonate, and mixtures thereof. Commercially available initiators are obtainable under trade names such as Trigonox® 99, Trigonox® SBP, Trigonox® EHP, Trigonox® 131, Trigonox® 141, Trigonox® 21S, and Perkadox® 16, Trigonox® 27, Trigonox® 22, Trigonox® 29, Trigonox® 25, Trigonox®
30 125, Trigonox® 121, Trigonox® 421, Trigonox® 425, Perkadox® AMBN, Perkadox® AIBN, Perkadox® L W-75, Perkadox® 12, and Laurox.

The "second" initiators that are used can be classified on the basis of their half-lives as determined by conventional thermal decomposition studies in monochlorobenzene, as is known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel), and in accordance with the principles as set out above. The "second" initiator is different to the "first" initiator, although it may be selected from the same group as described for the "first" initiator.

By dosing the "second" initiator, the same or lower residual level of monomers can be achieved compared to a conventional process that differs in that the initiators are not dosed and optimized on the dosing process.

When the reaction mixture is formulated at or near the polymerization temperature, which is called the warm-start process, it is not required to add a certain amount of "first" initiator before bringing the reaction mixture to the reaction temperature and dosing the remainder at the reaction temperature. However, also in this warm-start process it can be beneficial to add at once up to 5 wt.%, preferably up to 10 wt.% of the "first" initiator, based on the combined weight of the monomers, to the reaction mixture prior to polymerization, and to dose the remainder of the "first" initiator continuously or semi-continuously at the reaction temperature. When this procedure is used, the "first" initiator is added as the last ingredient after having mixed the monomers, solvent, and possibly other components. This procedure is particularly preferred if a certain amount of polymerization inhibitor (a radical trapping species) is present in the reaction mixture. If such radical scavenger is present, for instance because it is contained in the monomer as a constituent thereof (typically added as a stabilizer) the initially dosed initiator will react with said scavenger, thereby preventing a delayed start of the polymerization reaction. It is noted that in this procedure, the only exception to the rule that "first" initiator is added as the last ingredient is that "second" initiator may be added even after addition of all "first" initiator.

Preferably, the type and amount of "second" initiator is selected such that the residual monomer content of the final polymerized product is less than 5000 mg/kg of monomer, preferably less than 2000 mg/kg of monomer, more preferably less than 1000 mg/kg of monomer.

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The total amount of "first" and "second" initiator to be used in the process according to the invention is within the range conventionally used in polymerization processes. Typically, it is preferred to use at least 0.01 wt.%, more preferably at least 0.05 wt.%, and most preferably at least 0.1 wt.% of all initiators and preferably at most 5 wt.%,
10 more preferably at most 3 wt.%, and most preferably at most 1 wt.% of all initiators, based on the weight of the monomers to be polymerized.

The one or more "first" initiators are dosed to the reactor as such or as a mixture with one or more solvents. Suitable solvents are preferably selected from the group
15 consisting of water, conventional organic solvents, monomers, blowing agents (such as pentane, isopentane, and the like), and mixtures thereof. Preferably, suspensions are used, such as a 40 wt.% dibenzoylperoxide suspension in water. Such a suspension product can be obtained commercially from Akzo Nobel Polymer Chemicals under the trade name Perkadox® L W-40. When solvents such as alcohols
20 are used, they can be removed during working up the polymer after the process of polymerization. Furthermore, it is advantageous to use solvents that do not adversely affect the thermal stability of the initiator dissolved therein, as can be verified by analyzing the half-life temperature (temperature at which the half-life is 1 h) of the initiator in said solvent. An example of such solvent is isododecane. If a dispersion of a
25 "first" initiator is dosed, the dispersion can be a dispersion of the initiator as such or a dispersion of a solution of said "first" initiator. Preferably, the dispersion is an aqueous dispersion, for instance having an initiator concentration of 0.1 to 60 wt.%, more preferably 0.5 to 25 wt.%, and most preferably 2 to 15 wt.%. Dilute initiator solutions or dispersions ensure rapid mixing of the initiator and the polymerization mixture, which
30 leads to a more efficient use of the initiator, which is crucial for the fast initiators that

may be used. In case "second" initiator is also dosed to the reaction mixture it may be added as described above for "first" initiator.

5 The polymerization process can be conducted either as a solution process wherein the reaction mixture is a mixture of monomers with a solvent or as a suspension process wherein the reaction mixture typically is a suspension of monomers in (usually) water, or as an emulsion or micro-emulsion process wherein the monomers typically are emulsified in water. In these processes the usual additives may be used. For example, if the monomer is present in the form of a suspension in water, one or
10 more of the usual additives like a surfactant, a chain transfer agent, protective colloid, anti-fouling agent, pH-buffer, flame retardants, flame retardant synergists, etc., may be present. Blowing agents can be added at the start or during the polymerization process. Because of the presence of styrene monomer and blowing agents such processes are at least partially carried out in a pressurized reactor. The combined
15 weight of the additives preferably is at most 20 wt.%, based on the combined weight of all monomers.

The preferred process according to the invention is a suspension process that is carried out batchwise. More preferably, it is a batchwise suspension process making
20 expandable polystyrene (EPS).

In addition to the fact that addition of "first" initiator (and "second" initiator in the case "second" initiator is actually dosed) at variable rate is beneficial for using the cooling capacity of the polymerization reaction in the most optimal way, it was also found that
25 varying the dosing speed of "first" initiator (and "second" initiator) during the polymerization process is advantageous for obtaining an economical polymerization process and obtaining polymerized product with the desired molecular weights. By varying the dosing speed within one run, polymers with a polymodal molecular weight distribution can be made. For instance, a bimodal molecular weight distribution can be
30 made in the same run by using two periods with varying dosing speeds. Such bimodal molecular weight distributed polymer mixture has a part with low-molecular weight that

is useful for improving the expandability of polystyrene and a part with high-molecular weight that improves the mechanical properties of the polymer. The continuous or semi-continuous dosing can also be done using a mixture of two or more "first" initiators (and a mixture of two or more "second" initiators).

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Furthermore, it was observed that a polymer with essentially the same molecular weight as from a conventional process can be produced in less time, the only difference in the process being the controlled dosing of the "first" initiator and optimizing the initiators on the dosing process.

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After the polymerization, the resulting (co)polymer (or resin) will be treated as is usual in the art. Polymers so obtained can be submitted to the usual monomer reduction, drying, and/or screening steps. These one or more steps could be followed by, for example, an expansion step. As in conventional EPS processes, the amount of residual monomer content in the polymer product can be reduced in the usual manner; for instance by an after-treatment comprising a heat treatment step at approx. 110-170°C in the presence of "second" initiators with half-life temperatures as defined before, such as tert-butylperoxybenzoate, tert-butyl peroxy-2-ethylhexyl carbonate, dicumylperoxide, or tert-amyl peroxy-2-ethylhexyl carbonate, which are added at the start or during the polymerization process. The resulting resin is characterized in that it preferably contains less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably, less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening.

The resulting resin is further characterized in that it preferably has a Mw of at least 100,000 g/mol, more preferably of at least 125,000 g/mol, and most preferably of at least 150,000 g/mol, and that it has a Mw preferably of at most 500,000 g/mol, more preferably of at most 450,000 g/mol, and most preferably of at most 350,000 g/mol, measured in accordance with conventional gel permeation chromatography techniques using polystyrene standards.

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The invention further relates to styrene based (co)polymer obtainable by the hereinbefore-mentioned process and to the use of the styrene (co)polymer in a shaping process involving the heating of the co(polymer) for the preparation of foamed articles.

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The invention is illustrated with the following non-limitative examples.

Examples 1-4 and Comparative Examples A-D

10 General for Experiments 1-4 and A-D:

BPO (Perkadox® L W-75) Dibenzoyl peroxide ("first" initiator) ex Akzo Nobel
 Tx-117 (Trigonox® 117) Tert-butylperoxy 2-ethylhexylcarbonate ("second" initiator) ex Akzo Nobel
 Tx-131 (Trigonox® 131) Tert-amylperoxy 2-ethylhexylcarbonate ("second" initiator) ex Akzo Nobel

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A temperature-controlled 1-liter stainless steel Büchi reactor provided with a baffle, a three-blade stirrer, a pressure transducer, an initiator dosing line(s), and a nitrogen purge was charged with 1.25 g of tricalcium phosphate. Then a solution of 230 g of water, 20 g of a 0.1 wt.% Nacconol® 90G (ex Stephan Chemie Co.) solution in water and 10 g of a 0.5 wt.% Gohsenol® C500 (ex Nippon Gohsei) solution in water were added and stirred for approximately 5 min. To the reactor 220 g of styrene monomer was added. The reactor was evacuated several times to remove oxygen, a nitrogen blanket was applied, and the reactor was closed. The initial temperature of the reactor content was raised from ambient to 110°C or 90°C, for Examples 1-4 and Comp. Examples A-D, respectively, in 45 minutes and the reactor was pressurized. In Comp. Examples A-D: After 225 minutes the temperature was raised to the polymerization temperature of 120°C over a period of 60 minutes. This temperature was maintained for 120 minutes. Then, it was cooled to room temperature. In Examples 1-4 the initiator was dosed, using a pressure pump. In examples where no pentane was used, both "first" and "second" initiator were dosed in 90 minutes as a solution in styrene. In examples where pentane was used, "first" initiator (BPO) was added as a solution in

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styrene and pentane (30g/20g) and "second" initiator was added as a solution in just pentane. After 190 min at 110°C the temperature was increased to 120°C in 30 minutes. The "second" initiator" was added to the polymerization reaction 190 minutes after the start of the reaction as one portion or dosed over a period of 15 minutes. This

5 temperature was maintained for 60 minutes. Then, it was cooled to room temperature

The results are collected in the table below. It can be concluded that with dosing of "first" initiator (Examples 1-4), EPS with the same molweight (Mw and Mn) and polydispersity can be obtained as compared to examples wherein "first" initiator is not dosed (Comp. Examples A-D). In dosing experiments wherein no pentane is used

10 (Examples 3-4) also the same low residual styrene values are obtained as compared to non-dosing examples wherein no pentane is used (Comp. Examples C-D).

[illegible]

Examples 5-9 and Comparative Example E:

	Px-L W-75	(Perkadox®-L W-75) Dibenzoyl peroxide ("first" initiator) ex Akzo Nobel
5	Px-L W-40	(Perkadox®-L W-40) Dibenzoyl peroxide ("first" initiator) ex Akzo Nobel
	Px-BC	(Perkadox® BC-FF) Dicumyl peroxide ("second" initiator) ex Akzo Nobel
	Tx-117	(Trigonox® 117) Tert-butylperoxy 2-ethylhexylcarbonate ("second" initiator) ex Akzo Nobel
10	Tx-131	(Trigonox® 131) Tert-amylperoxy 2-ethylhexylcarbonate ("second" initiator) ex Akzo Nobel

A temperature-controlled 1-liter stainless steel Büchi reactor provided with a baffle, a three-blade stirrer, a pressure transducer, an initiator dosing line(s), and a nitrogen purge was charged with 1.25 g of tricalcium phosphate. Then a solution of 260 g of water, 20 g of a 0.1 wt.% Nacconol® 90G (ex Stephan Chemie Co.) solution in water and 10 g of a 0.5 wt.% Gohsenol® C500 (ex Nippon Gohsei) solution in water were added and stirred for approximately 5 min. To the reactor 250 g of styrene monomer was added. The reactor was evacuated several times to remove oxygen, a nitrogen blanket was applied, and the reactor was closed.

20 The initial temperature of the reactor content was raised from ambient to 110°C or 90°C, for Exp. 5-9 or Comp. Exp. E, respectively, in 45 minutes and the reactor was pressurized. If the initiator was dosed, a pressure pump was used for dosing. Both "first" and "second" initiator were added as a solution in styrene. In Example 5, 8, and 9, "second" initiator was added to the polymerization reaction 180, 160, 25 and 135 minutes, respectively, after the start of the reaction. In Examples 6, 7, and E, "second" initiator was added at once prior to the start of the polymerization. The results are collected in the table below. It can be concluded that the polystyrene obtained in a polymerization process according to the invention is comparable with respect to molecular weight and molecular weight distribution as 30 compared to polystyrene obtained in a conventional process, but the process of the invention requires shorter polymerization time.

(Comparative) Example	5	6	7	8	9	E
1 st initiator	Px-L W75	Px-L W75	Px-L W75	Px-L W75	Px-L W75	Px-L W75
2 nd initiator	Tx-131	Tx-117	Tx-BC	Tx-131	Tx-131	Tx-117
Mw product (x 1000) g/mol	260	229	231	284	279	243
Mn product (x 1000) g/mol	84	75	72	92	102	101
D (Mw/Mn)	3.1	3.1	3.2	3.1	2.8	2.7
Residual styrene (w/w%)	0.28	0.10	0.50	0.17	0.07	0.31
Polymerization time	300	370	325	300	300	480
Amount 1 st initiator (meq/100g styrene)	1.24	0.83	1.53	1.24	0.98	0.98
Dosing time 1 st initiator (min)	90	90	90	75	80	0
Amount 2 nd initiator (meq/100g styrene)	0.46	0.87	0.46	0.46	0.46	0.46
Dosing time 2 nd initiator (min)	15	0	0	5	5	0
Initial temperature (°C)	110	110	110	110	110	90
Max. polymerization temperature (°C)	120	150	130	120	120	120

Claims

1. Process for polymerizing styrene monomer for the preparation of styrene-
5 containing (co)polymers, wherein the process comprises the steps of
continuously or semi-continuously dosing "first" initiator to a composition
comprising said styrene monomer and addition of "second" initiator which is
different to the "first" initiator, wherein the process is not a process for
10 producing expandable styrene-based polymer beads, which comprises
adding a low temperature polymerization initiator to an aqueous medium
having suspended therein blowing agent-containing expandable styrene-
based polymer small particles whose particle sizes have been adjusted so
as to have a particle size distribution falling within a mean particle size of
15 about 20% in a proportion of at least half the amount required for
polymerization of a styrene-based monomer to be added to the system,
adding a blowing agent to the system in an amount enough to inhibit
expansion of said expandable styrene-based polymer small particles while
the system is heated to a temperature for first stage polymerization,
20 continuously or intermittently adding thereto a styrene-based monomer to
which the rest, if any, of said low temperature polymerization initiator and a
high temperature polymerization initiator.
2. Process according to claim 1 wherein the composition further comprises
25 co-monomers selected from the group consisting of vinylidene chloride,
vinyl acetate, ethylene, propylene, acrylonitrile, butadiene, (meth)acrylates,
and ethylenically unsaturated polymers, such as polybutadiene and styrene
butadiene rubber.
3. Process according to claim 1 or 2 wherein "first" initiator is dosed
30 continuously or semi-continuously from the point in time at which at least
1%, preferably at least 0.5%, more preferably at least 0.1%, most
preferably none of the monomers have already been polymerized until at

least 70%, preferably at least 80%, more preferably at least 90%, and most preferably essentially all of the monomer is polymerized, the term "essentially all of the monomer is polymerized" meaning that less than 1000 ppm of monomer is present in the final polymerized product.

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4. Process according to any one of claims 1-3 wherein the "first" initiator is selected from the group consisting of mono-, bi-, and poly(peroxy and/or azo)functionalized peroxydicarbonates, peroxycarbonates, peroxyesters, peroxyketals, diacylperoxides, dialkylperoxides, ketone peroxides, azo-initiators, and mixtures thereof, optionally further functionalized with amines, phosphates, esters, ethers, alcohols, etc., which "first" initiators are preferably selected from the group consisting of dilauroyl peroxide, dibenzoylperoxide, tert-butyl peroxyperpivalate, tert-amyl peroxy perpivalate, azobis(isobutyro)nitrile, azobis(2-methylbutyronitrile), tert-butyl peroxy-2-ethylhexanoate, tert-amyl peroxy-2-ethylhexanoate, tert-butyl peroxydiethylacetate, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(tert-butylperoxy)cyclohexane, cumyl peroxyneodecanoate, di(sec-butyl) peroxyneodecanoate, di(2-ethylhexyl) peroxydicarbonate, 2,5-dimethyl-2,5-di(2-ethylhexanoylperoxy)hexane, 1,1,3,3-tetramethylbutyl peroxyperpivalate, 1,1,3,3-tetramethylbutyl peroxyneodecanoate 2,2-di[4,4-di(tert-butylperoxy)cyclohexyl]propane, and tert-amylperoxy-2-ethylhexyl carbonate, and mixtures thereof.
5. Process according of any one of claims 1-4 wherein the reaction temperature is 170°C or lower, preferably 150°C or lower, more preferably 130°C or lower, and most preferably 120°C or lower.
6. Process according to any one of claims 1-5 wherein at least part of the initiator is continuously or semi-continuously dosed over a period of at least 0.5 hour, preferably at least 1 hour.

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7. Process according to any one of claims 1-6 wherein at least 0.01 wt.%, more preferably at least 0.05 wt.%, and most preferably at least 0.1 wt.% of combined weight of all initiators and preferably at most 5 wt.%, more preferably at most 3 wt.%, and most preferably at most 1 wt.% of combined weight of all initiators, based on the weight of the monomers to be polymerized, is used.
8. Process according to any one of claims 1-7 wherein at least 50 wt.% of the mixture of monomers consists of styrene monomers.
9. Process according to any one of claims 1-8 wherein the process is a batchwise suspension process.
10. Process according to claim 9 for the preparation of expandable polystyrene.
11. Styrene based (co)polymer obtainable by a process according to any one of claims 1-10, wherein the styrene based (co)polymer has less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably, less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening.
12. Use of a styrene (co)polymer according to claim 11 in a shaping process involving the heating of the co(polymer) for the preparation of foamed articles.

Abstract

The invention relates to a process for polymerizing styrene monomer for the preparation of styrene-containing (co)polymers, wherein the process comprises the steps of continuously or semi-continuously dosing "first" initiator to a composition and addition of "second" initiator which is different to the first initiator.

5 The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.